Evidence for Mercurinium Ion by means of Nuclear Magnetic Resonance

By YASUKAZU SAITO* and MASASHI MATSUO
(*Department of Synthetic Chemistry, University of Tokyo, Hongo, Tokyo, Japan*)

AN olefin–mercury(II) π-complex, *i.e.*, mercurinium ion, has long been postulated as the reaction intermediate in oxymercuration or deoxymercuration.[1] Recently, Reutov *et al.*[2] directly observed by n.m.r. the cyclohexene–mercury(II) π-complex, but the spectrum presented by them was too unresolved to give the adequate evidence of π-complexing. We report our interpretation of the n.m.r. spectrum† of ethylene–mercury(II) π-complex, determined in aqueous mercuric nitrate solution at room temperature.

On addition of ethylene to aqueous mercuric nitrate at room temperature, the 2-hydroxyethylmercury(II) complex was formed. Its n.m.r. spectrum has been analysed as an A_2X_2 spin system.[3] Besides the A_2X_2 peaks due to this complex, another set of triplet-like peaks has been found at τ 6·29 with respect to internal acetone (τ 7·83). When ethylene is dissolved in aqueous mercuric acetate, the n.m.r. spectrum shows no triplet-like peaks and only the A_2X_2 pattern was observed. Undoubtedly there exists a new material in that solution, which contains ethylene. Moreover, satellites due to ^{199}Hg ($I = \frac{1}{2}$, natural abundance 16·84%) are observed for the triplet-like peaks as well as for the A_2X_2 peaks. This new material must be a mercury complex.

Many olefin–metal ion π-complexes have been studied by n.m.r.[4] The chemical shifts of olefinic protons are dependent on the π-complexing metal ion, but generally the chemical shifts of the complexed olefins are at a higher field than those of the free olefins. Thus, the proton–^{195}Pt spin-coupling constants in olefin–platinum(II) π-complexes are almost comparable in magnitude to those of alkyl–platinum(II) complexes. For example, the magnitude of J(H–^{195}Pt) for $K[(CH_2{:}CH_2)PtCl_3]$ in acetone was reported as 66·8 c./sec.,[5] whereas J(H–^{195}Pt) for $[Me_3Pt]NO_3$ in water and for $[Me_3PtI]_4$ in chloroform were found to be 77·3,[6] and 77·5 c./sec.,[7] respectively. For the 'new' mercury complex, the values J(H–^{199}Hg) = 247 c./sec. and τ 6·29 were obtained. Since the coupling constant between ^{199}Hg and the α-proton of the 2-hydroxyethylmercury(II) complex in the same solution was 271 c./sec., this magnitude, 247 c./sec., may be reasonable for a π-complex. The chemical shift, 6·29 p.p.m., is also reasonable, if τ 6·41 for $K[(CH_2{:}CH_2)PtCl_3]$ in acetone[5] is considered. Moreover, the triplet-like pattern can be interpreted in terms of the A_2B_2 spin system,[8] in which the chemical shift difference between A and B is small in comparison with the proton–proton coupling constants. We conclude, therefore, that the triplet-like pattern is due to the ethylene–mercury(II) π-complex, and that the observed spin system of A_2B_2 suggests that the protons of this π-complex are not completely equivalent.

---

† The C-60 n.m.r. spectrometer of Japan Electron Optics Laboratory Co., Ltd. was used. All reagents were of G.R. grade.

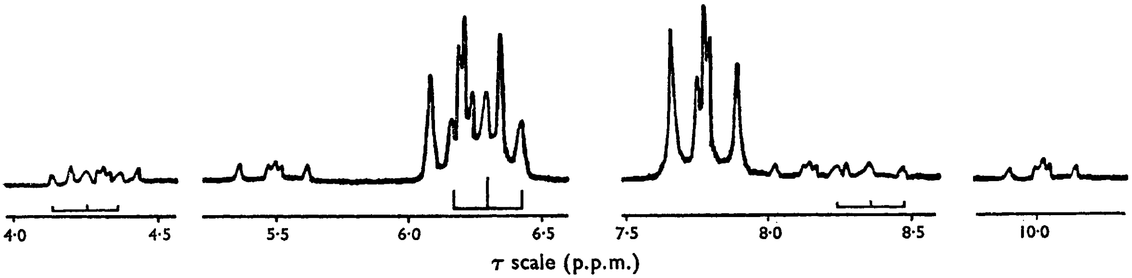

FIGURE. *The* 60 *Mc./sec. n.m.r. spectrum of the* Hg-$(NO_3)_2$–D_2O *solution* (2 M) *containing ethylene at room temperature.*

No change in the n.m.r. spectrum occurred on heating the solution to 60°. When dilute hydrochloric acid was added at room temperature, both the π- and σ-complexes were diminished to the same extent. Since the addition of either potassium hydroxide or lithium nitrate increased the relative concentration of the π-complex, the formation of mercurinium ion seems to be more favoured in the solution with greater ionic strength.

The authors express their gratitude to Professor Yukio Yoneda for helpful discussions.

(*Received, July* 31*st*, 1967; *Com.* 795.)

---

[1] J. Chatt, *Chem. Rev.*, 1951, **48**, 7.
[2] V. I. Sokolov, Yu. A. Ustnyuk, and O. A. Reutov, *Doklady Akad. Nauk S.S.S.R.*, 1967, **173**, 1103.
[3] P. R. Wells, and W. Kitshing, *Tetrahedron Letters*, 1963, **1531**.
[4] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1.
[5] H. P. Fritz, K. E. Schwarzhans, and D. Sellmann, *J. Organometallic Chem.*, 1966, **6**, 551.
[6] J. A. Smith, *J. Chem. Soc.*, 1962, 4736.
[7] G. L. Morgan, R. D. Rennick, and C. C. Soong, *Inorg. Chem.*, 1966, **5**, 372.
[8] K. B. Wiberg and B. J. Nist, "The Interpretation of N.m.r. Spectra", W. A. Benjamin, New York, 1962, pp. **365** and **464**.